



# Impacts of Alternative Fuels on Air Quality

## Subcontractor

University of Dayton Research Institute

## Principal Investigator

Philip H. Taylor  
Barry Dellinger  
University of Dayton Research Institute  
300 College Park  
Dayton, OH 45469-0132  
(513) 229-2846

## DOE Project Manager

Michael Gurevich  
U.S. Department of Energy  
CE-332, MS6A-116/Forrestal  
1000 Independence Avenue, SW  
Washington, DC 20585  
(202) 586-6104

## NREL Technical Monitor

Michelle Bergin  
NREL  
1617 Cole Boulevard  
Golden, CO 80401-3393  
(303) 275-4429

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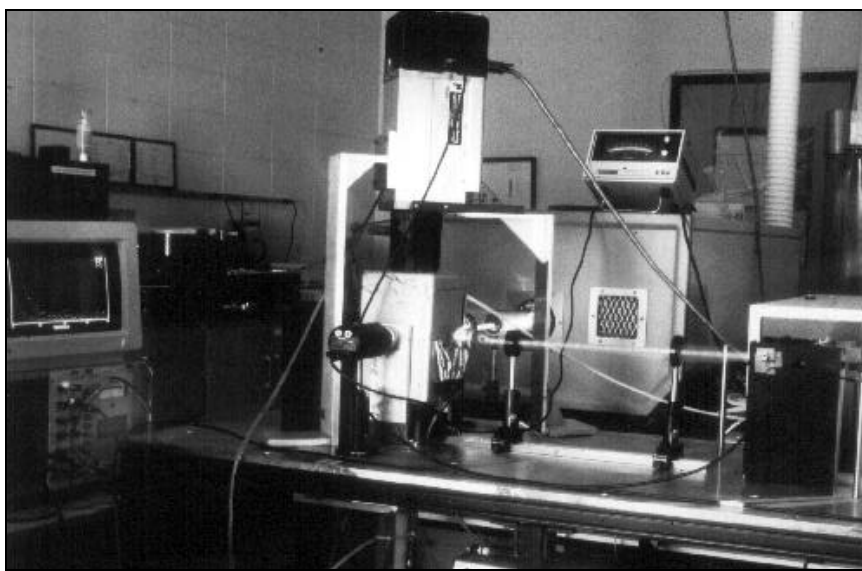
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## NREL Subcontract Administrator

Kathleen Roque (303) 275-3124

## Objectives

- Identification of systematic error in previous low-temperature measurements and augmentation of the alternative fuel-hydroxyl radical (OH) reaction kinetic database.
- Identification of multiple mechanisms of reaction and any change in mechanism with temperature.
- Improvement of application of transition state theory (TST) and structure activity relationship (SAR) formalism to modeling of bimolecular reactions over extended temperature ranges.



*The UDRI Laser Photolysis/Laser-Induced Fluorescence (LP/LIF) System*

## Approach

A refined laser photolysis/laser-induced fluorescence (LP/LIF) technique is used for the measurement of OH-alternative fuel reaction kinetics over an extended temperature range. The dual laser system results in high precision rate coefficient measurements and minimization of systematic errors. The major advantages of this technique are:

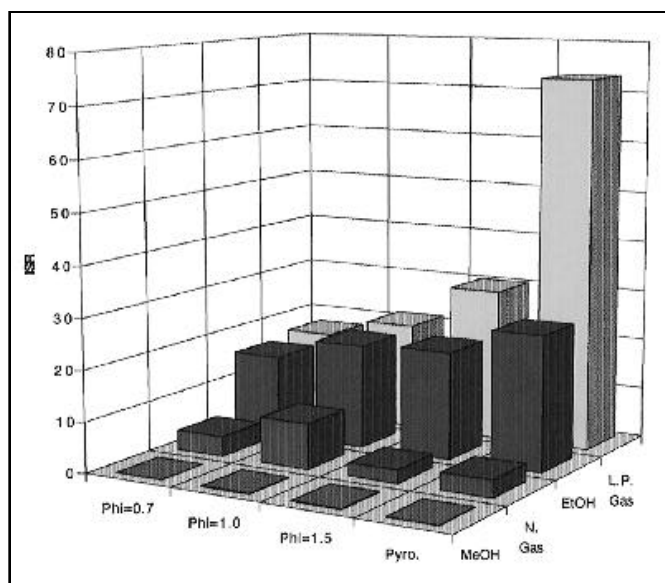
- Capability to measure reaction rate constants over an extended temperature range using a single apparatus.
- Generation of a clean source of OH radicals.
- Capability of atmospheric pressure measurements.
- Extensive purification and analysis of all reactants.
- Capability to thoroughly analyze potential photolysis-based secondary reactions.

## Accomplishments

Rate measurements were obtained for the reaction of hydroxyl radical (OH) with alternative fuel combustion by-products over an extended temperature range. New measurements are reported for methanol, ethanol, dimethyl ether, methyl *t*-butyl ether, and acetaldehyde. Room-temperature rate coefficients for methanol,



ethanol, and dimethyl ether were in excellent agreement with previous measurements. Room- temperature rate coefficients were ~20% lower and ~20% higher than previous measurements for acetaldehyde and methyl *t*-butyl ether, respectively. For methanol, ethanol, dimethyl ether and methyl *t*-butyl ether, substantial curvature in the



Arrhenius plot of OH-acetaldehyde rate coefficient measurements. Also shown are previous measurements and the recommendation of Atkinson

Arrhenius plots was observed. The temperature-dependent data for methanol, ethanol, dimethyl ether and methyl *t*-butyl ether are consistent with a H-atom abstraction mechanism. Experimental measurements of the acetaldehyde—OH reaction indicated a complex reaction mechanism. QRRK analyses indicated that OH addition followed by  $\text{CH}_3$  elimination was the dominant reaction pathway at temperatures between 295 and 600 K. The experimental and modeling results further indicated that the dominant reaction channel at combustion temperatures is H-atom abstraction from the  $\text{CH}_3$  group.

## Future Direction

Future measurements will include product determinations for the OH-acetaldehyde reaction and additional rate measurements for OH and NO reactions with alternative fuel combustion by-products. A time-of-flight mass spectrometer will be used for the product determinations.

Arrhenius plot of OH-acetaldehyde rate coefficient measurements. Also shown are previous measurements and the recommendation of Atkinson.

## Publications

Taylor, P.H., M. Sm. Rahman, and B. Dellinger. 1996. *Impacts of Alternative Fuels on Air Quality*. NREL/TP-XXX-XXXX. National Renewable Energy Laboratory, Golden, CO.

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